# PATENT SPECIFICATION

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The Inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are: RUDOLF MARTEN, Roggendorfstrasse 51, Koeln-Flittard, Germany, Otto Bayer, Carl-Rumpff-Strasse 79, Leverkusen, Germany, both German Citizens.

#### COMPLETE SPECIFICATION

## A Process for production of Isocyanate Polyaddition Products

We, FARBENFABRIKEN BAYER ARTIEN-GESELLSCHAFT of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of synthetic plastics, including foamed polyurethanes by the isocyanate polyaddition process.

The present invention provides a process for the production of synthetic plastics, which comprises reacting at least one polyester containing active hydrogen atoms (as determined by the Zerewittenof method) with one or more organic polyisocyanates, wherein the polyester is the addition product of a primary or secondary amine to a double bond which is in the α: β-position to an ester group of an α,β-unsaturated polyester.

As used herein the term " $\alpha,\beta$ -unsaturated polyester" means a polyester containing at least one double bond in a position  $\alpha,\beta$ - to an ester group.

The addition of the primary or secondary amines to the  $\alpha,\beta$ -unsaturated polyesters leads to the formation of modified polyesters which show an increased reactivity in reaction with isocyanates because of the presence of the secondary or tertiary amino group and generally do not require an amine catalyst, for [Price 4s. 6d.]

example during foaming. Secondary amino groups react very quickly with the isocyanate component and, for example when producing a foam material, lead to a stabilisation of the foaming process, and when producing lacquers and moulded elements, lead to a more rapid curing.

The addition products of the primary and secondary amines to the  $\alpha,\beta$ -unsaturated polyesters are produced in a manner known per se.

The  $\alpha,\beta$ -unsaturated polyesters required for this purpose can be obtained by esterifying or transesterifying an  $\alpha,\beta$ -unsaturated monocarboxylic and/or polycarboxylic acid or derivatives thereof, if desired together with other saturated monocarboxylic and/or polycarboxylic acids, with polyhydric alcohols. The esterification is carried out under the usual conditions, for example at 130—210° C. with the addition of stabilisers (such as tert. butyl pyrocatechol or hydroquinone) under an inert gas and/or in the presence of esterifying or transesterifying catalysts.

For the introduction of the  $\alpha_x\beta$ -unsaturated carboxylic acid ester function, various types of  $\alpha_x\beta$ -unsaturated monocarboxylic and/or polycarboxylic acids and their derivatives can be used, such as maleic acid, fumaric acid, maleic acid anhydride, maleic acid dimethyl ester, fumaric acid diethyl ester, itaconic acid, aconitic acid, chloromaleic acid, acrylic acid, ethyl acrylate, methacrylic acid, mesaconic acid, citraconic acid and glutaconic acid.

As well as  $\alpha, \beta$ -unsaturated carboxylic acids, it is possible in addition to use other saturated and unsaturated carboxylic acids in the esterification, such as succinic, sebacic, adipic, glutaric, azelaic, phthalic, isophthalic, terephthalic, trimellitic acids, dimerised and trimerised unsaturated fatty acids, oleic stearic, ethyl caproic acids, technical fatty acid mixtures such as tall oil, train oil or linseed oil

10 fatty acids.

Examples of polyhydric alcohols for the esterification are dihydric and higher polyhydric alcohols of aliphatic, cycloaliphatic, aromatic or heterocyclic nature, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycols, propylene glycol, dipropylene glycol, tripropylene glycol, propane-1,3-diol, butane-1,2-diol, butane-1,3diol, butane-1,4-diol and butane-2,3-diol, hexane-2,5-diol or hexane-1,6-diol, octadecane diol and octadecene diol, butene-1,4-diol and butine-1,4-diol, glycerine, trimethylol ethane, trimethylol propane, pentaerythritol, hexane triols, mannitol, sorbitol, glucose, fructose, mannose, cane sugar, invert sugar, solutions of invert sugar in polyalcohols, degraded starches, cyclohexane - 1,4 - dimethanol, hydroxyalkylated hydroquinone or diphenylol alkanes, and also amino alcohols such as triethanol-30 amine, hydroxyalkylated ethylene diamines or phenylene diamines. The polyhydric alcohols used can also be of relatively high molecular weight, such as castor oil, polyethylene glycols of molecular weight 400, 600 or 2009, polypropylene glycol ethers or the adducts of propylene oxide and polyfunctional starting molecules with molecular weights up to 3000. In addition, polyesters produced by copolymerisation of anhydrides with alkylene oxides according to U.S.A. Specification No. 2,822,350 can also be used.

The proportions used in the production of the polyester are so chosen that the  $\alpha_2\beta$ -unsaturated polyesters have a low acid number, as far as possible below 20; it is also possible to use stoichiometric quantities of acids and alcohol in those cases in which the polyfunctional nature of the molecule is produced by a modification with primary amines or polyamines. In general, the esters should contain at least one unsaturated grouping per molecule. A low amine content is advantageous when producing soft foam materials, whereas high amine contents and branches may be 55 advantageous with hard foam materials.

Amines of different natures are used for modifying the polyesters, temperatures of 20-80° C. generally being employed for the addition of the primary amines and tempera-60 tures of 20—140° C. with secondary amines. If required, the modification is also effected in inert solvents, e.g. alcohols such as methanol or aliphatic or aromatic hydrocarbons.

Monoamines and/or polyamines can be 65 used as the amines for addition to the  $\alpha_2\beta_-$ 

compounds with unsaturated polyesters; several amino groups can react several times, depending on the reaction conditions and proportions. The following are mentioned as examples of the amines: methylamine, ethylamine, butylamine, allylamine, octadecylamine, tallamine, isobutylamine, cyclohexylamine, ethanolamine, B-amino-propionitrile, aniline, toluidines, aminodiphenylmethanes, furfurylamine, aminopyridines, condensation 75 products of fatty acids and diethylene triamine or triethylenetetramine, ethylene diamine, hexamethylene diamine, p-phenylene diamine, hexahydro - p - phenylene diamine, hydrogenation products of the adducts of acrylonitrile and monohydric alcohols and polyhydric alcohol, monoamines and polyamines, toluylene-diamines, dimethylaminedibutyl amines, dierhanolamine, pyrrolidine, piperidine and morpholine. Amines with a 85 pronounced basic character are advantageous.

The proportions between amine and  $\alpha_s\beta$ unsaturated groupings are so adjusted that up to 100-mol% of amine, based on as B-unsaturated groupings, are introduced. With 90 polyamines, higher proportions of amine can

be used.

According to one particular form, addition products of primary amines which have also been reacted with alkylene oxides or with 95 a.B-unsaturated esters or nitriles can be used as secondary amines for the process according to the invention. For this purpose, the addition products which are obtained with primary amines and which contain secondary amino 100 groups may be modified with ethylene oxide, 1:2-propylene oxide, a butylene oxide or styrene oxide if desired at temperatures between 20 and 140° C. and possibly with concurrent use of inert solvents. Another possi- 105 bility of modification comprises the addition of for example acrylonitrile, methacrylonitrile, ethyl acrylate or ethyl methacrylate at temperatures of for example 50 to 120° C. By the use of such still further modified addition pro- 110 ducts, the mechanical properties of the plastics obtainable according to the invention can be varied.

According to another embodiment of the invention, the adducts of the amine with the 115 ester may have been reacted with an alkylation agent, for example with methyl iodide, benzyl chloride or diethyl sulphate. In this way, quaternary salts, for example, can be obtained and thus ionic groups which for example 120 impart improved water absorption and exchanger capacity to a foam material produced by the process of the invention with the use of an addition product modified in this

The polyesters thus obtained containing at least two reactive hydrogen atoms in the molecule, i.e. the starting materials for the process according to the invention, are light yellow to brown substances which are generally of 130

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low viscosity and which are reacted together with polyisocyanates and also possibly with chain extenders, cross-linking agents and/or blowing agents. They can also be mixed with other known polyhydroxyl compounds such as polyesters, polyethers, polythioethers, polyacetals, adducts of alkylene oxides and polyamines, polyphosphites according to Patent No. 998,859 and alkoxylated phosphoric acids.

Examples of polyisocyanates are aliphatic and aromatic polyisocyanates, for example alkylene diisocyanates (such as tetramethylene and hexamethylene diisocyanates) arylene diisocyanates and their alkylation products as well as the phenylene diisocyanates, naphthalene diisocyanates, diphenyl methane diisocyanates, toluylene diisocyanates, diisopropyl benzene and triisopropyl benzene diisocyanates and triphenyl methane triisocyanates, p-isocyanatophenylthiophosphoric acid triester, pisocyanatophenylphosphoric acid triester, aralkyl diisocyanates such as 1-(isocyanatophenyl)ethylisocyanate or the xylylene diisocyanates and also those polyisocyanates which have been reacted with less than stoichiometrically equivalent quantities of polyhydroxyl compounds and which are substituted by various substituents, such as OR, NO<sub>2</sub>, Cl, such as trimethylol propane, hexanetriol, glycerine and butanediol. Also to be mentioned are for example polyisocyanates masked with phenols or bisulphite, acetal-modified isocyanates and also polymerised isocyanates containing isocyanurate rings.

The quantities of polyisocyanate should generally be at least equivalent to the sum of reactive hydrogen atoms which are present. When using water as blowing agent, suitable quantities of excess isocyanate calculated also on the water content will be used. On the hand, excessive proportions isocyanate groups can be incorporated by polymerisation reactions or secondary addition reactions into the plastic structure. Instead of or in addition to the foaming with water, it is also possible to use other blowing agents such as azo-compounds, low-boiling hydrocarbons, halogenated methanes or ethanes or vinylidene chloride.

A foaming is preferably carried out in the presence of catalysts, for example amines such as triethylamine, dimethylbenzylamine, 1dimethylamino - 3 - ethoxy - propane, triethylene diamine or metal salts such as tin-55 (II) - acylates, dialkyl - tin - (IV) - acylates, acetyl - acetonates of heavy metals, or molybdenum glycolate. Other additives are emulsifiers, such as hydroxy ethylated phenols or biphenylols, higher sulphonic acids, sulphuric acid esters of castor oil or ricinoleic acid, ammonium salts of oleic acid, foam stabilisers such as alkylene oxide-silioxane copolymers, basic silicone oils or paraffins, and also dyestuffs, pigments and flame-proofing agents.

The foam materials are produced in a

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manner known per se by mechanical or manual mixing of the components and lead to excellent foam materials having high mechanical values, a low degree of brittleness, good adhesion, satisfactory pore structure and a low tendency to shrinkage.

The usual processes are likewise used in the production of synthetic plastics and lacquers, generally with the concurrent use of the conventional chain-extenders or cross-linking agents. Solid synthetic plastics can be obtained by preliminary extending with less or more than the equivalent quantity of polyisocyanate and subsequent vulcanisation with, on the one hand, polyisocyanate and, on the other hand, components which are poly-reactive with respect to isocyanate groups, such as water, polyalcohols, amino alcohols and polyamines. For the production of lacquer coatings, there are primarily used solutions of the polyisocyanates and of the polyesters to be employed according to the invention.

Examples of the production of the starting materials will now be given as mixes A—1 to A—30:

Esterification of the unsaturated acid or anhydride with the polyhydric alcohol was effected in each case under nitrogen in the presence of 0.2% of tert. butil pyrocatechol as stabiliser and 0.05% of titanium tetrabutylate as catalyst. The total time taken was 6 hours at the temperatures indicated and under the pressure conditions given. The amine was then added at 30-40° C. over a period of 2 hours, stirring was then carried 100 on for 2 hours at 40° C. and for another 2 hours at 75° C. 12 mm.Hg.

The parts indicated are parts by weight. In the determination of the OH-number, NHgroups are included. The amino esters pro- 105 duced contained no amide grouping according to the infra-red spectrum.

2120 parts of diethylene glycol, 980 parts of maleic acid anhydride, 170° C/100 110 mm.Hg; at 40° C., 1000 parts of cyclohexylamine; resulted in 2888 parts of light yellow aminoester:

Viscosity 5200 cP/25° C., 13.0% OH, acid number 12.4 3.52% N.

#### A 2

2400 parts of polyethylene glycol with a molecular weight of 200; 588 parts of maleic acid anhydride, 180° C./12 mm.Hg.; at 40° C., 580 parts of cyclohexylamine; resulted in 120 3440 parts of aminoester of dark brown colour:

Viscosity 1475 cP/25° C., 8.3% OH, acid number 3.1 2.34% N.

A 3125

848 parts of diethylene glycol, 392 parts of maleic acid anhydride, 445 parts of adipic

acid, 200° C./15 mm.Hg., 1485 parts of polyester (OH-number 59.7; acid number 0.5); 780 parts of this polyester were reacted at 50° C. with 198 parts of cyclohexylamine; resulted in 982 parts of yellowish aminoester: 5.0% OH, acid number 1.0.

A 4 1660 parts of linear polypropylene glycol (OH-number 270), 294 parts of maleic acid anhydride, 170° C./12mm. Hg.; 300 parts of cyclohexylamine at 40° C.; resulted in 2175 parts of aminoester: 4.6% OH, acid number 19.6 1.88% N.

A 5

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424 parts of diethylene glycol, 196 parts of maleic acid anhydride, 175° C./100 mm.Hg.; 210 parts of diethanolamine at 70° C., 2 hours 100° C. 4 hours 120° C.; resulted in 795 parts of aminoester:

Viscosity 1240 cP/25° C., 18.6% OH, acid

number 13.7 3.50% N.

A 6 848 parts of diethylene glycol, 196 parts of maleic acid anhydride, 630 parts of adipic acid, 200° C./12 mm.Hg; 144 g. of piperidine added at 70° C., 4 hours at 90° C., 4 hours at 120° C./12 mm.Hg.; resulted in 1575 parts of a light yellow aminoester: Viscosity 3840 cP/25° C. OH-number 150, acid number 1.3, 1.29% N.

A 7

1272 parts of diethylene glycol, 98 parts of maleic acid anhydride, 1460 parts of adipic acid, 200° C./m² mm.Hg.; 99 parts of cyclohexylamine added at 40° C.; resulted in 2540 parts of aminoester; OH-number 68.7, acid number 3.3, 0.52% N, viscosity 13,200 cP/25° C.

A 8 2000 parts of a linear polypropylene glycol (OH-number 112), 98 parts of maleic acid anhydride, 200° C./12 mm.Hg.; 90 parts of cyclohexylamine at 30° C.; resulted in 2165 parts of aminoester: Viscosity 603 cP/25° C., 45 OH-number 103, acid number 5.6 0.62% N, equivalent weight 2960.

A 9

a) 848 parts of diethylene glycol, 196 parts of maleic acid anhydride, 730 parts of adipic acid, 200° C./15 mm.Hg.; 1548 parts of polyester: Viscosity 8100 cP/25° C., OHnumber 75.8, acid number 3.5.

b) 780 parts of polyester A-9a, 85 parts of piperidine at 70° C., 2 hours 70° C., 2 55 hours 110° C./12 mm. Hg.; resulted in aminoester: Viscosity 10,7000 cP/25° C., OHnumber 92, acid number 3.8, 1.47% N.

A 10

780 parts of polyester A-9a, 95 parts of cyclohexylamine at 40° C.; resulted in 875 parts of aminoester: Viscosity 6150 cP/25° C, OH-number 132, acid number 3.7.

A 11

3600 parts of polyethylene glycol of the molecular weight 200, 882 parts of maleic acid anhydride, 170° C./12 mm.Hg. at 70° C., 400 parts of dimethylamine were introduced in 4 hours, 2 hours at 70° C.; 2 hours at 100° C. 2 hours at 110° C./12 mm.Hg.; resulted in 3170 g. of aminoester: Viscosity 1940 cP/25° C., 6.3% OH, acid number 2.4 0.73% N.

A 12

3000 parts of triethylene glycol, 980 parts of maleic acid anhydride, 170° C./65 mm.Hg.; 830 parts of aniline at 70° C., 2 hours at 70° C., 4 hours at 120° C./12 mm.Hg.; resulted in 4300 parts of aminoester: 9.7% of OH, acid number 6.7, 2.23 g' N. Viscosity 2565 cP/25° C. : T

A 13

600 parts of triethylene glycol, 196 parts of maleic acid anhydride, 170° C./60 mm.Hg.; 246 parts of imino - bis - propionitrile introduced dropwise at 90° C., 2 hours at 90° C., 85 6 hours at 120° C.; resulted in 1008 parts of aminoester: Viscosity 433 cP/25° C., 10.3% OH, acid number 8.4, 8.25% N.

A 14

134 parts of trimethylol propane, 1802 parts of diethylene glycol, 2080 parts of adipic acid, 98 parts of maleic acid anhydride, 200° C./12 mm.Hg.; 93 parts of cyclohexylamine at 40° C.; resulted in 3130 parts of aminoester: Viscosity 2840 cP/25° C., OH-number 95 149, acid number 1.0, 0.44% N.

A 15

648 parts of diethylene glycol, 490 parts of maleic acid anhydride, 170° C./100 mm.Hg.; 450 parts of cyclohexylamine at 40° C.; 100 resulted in 1533 parts of aminoester: 8.7% OH, acid number 43. 4.14% N.

A 16 1000 parts of polyethylene glycol of the average molecular weight 200, 392 parts of 105 maleic acid anhydride, 175° C./12 mm.Hg; 380 parts of cyclohexylamine at 40° C.; resulted in 1700 parts of aminoester: Viscosity 23,200 cP/25° C., 6.5%, OH, acid mumber 12.9, 3.14% N.

A 17

424 parts of diethylene glycol, 260 parts of itaconic acid, at 170° C./100 mm.Hg.; 214

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parts of benzylamine at 40° C.; resulted in 810 parts of aminoester: Viscosity 3290 cP/25 C., 13.1% OH, acid number 17, 3.5% N.

#### 5 A 18

360 parts of butane-1,4-diol, 260 parts of itaconic acid, 170° C./100 mm. Hg.; 108 parts of n-propylamine at 40° C.; resulted in 639 parts of aminoester: Viscosity 740 10 cP/25° C., 11.6% OH, acid number 14, 3.75% N.

#### A 19

368 parts of glycerine, 232 parts fumaric acid at 70° C./50 mm.Hg.; 118 parts of propylamine at 40° C.; resulted in 636 parts of aminoester: 24.8% OH, acid number 4.1, 4.25% N.

#### 75 A 20

440 parts of an adduct of 1:2 propylene 20 oxide and trimethylol propane (OH-number 3.2), 3000 parts of a linear polypropylene lycol (OH-number 112) and 294 parts of maleic acid anhydride, 200° C./12 mm.Hg.; . 30 parts of cyclohexylamine at 40° C.; 25 resulted in 3960 parts of aminoester: 3.5% OH, acid number 3.2, 1.02% N.

#### ·A 21

318 parts of diethylene glycol, 196 parts of maleic acid anhydride, 170° C./80 mm.Hg.; 30 200 parts of cyclohexylamine at 40° C.; resulted in 684 parts of aminoester: Viscosity 29,850 cP/25° C., 10.6% OH, acid number 17, 4.25% N.

#### A 22

800 parts of aminoester according to A 1, 112 parts of 1:2 propylene oxide introduced dropwise at 80° C., 2 hours at 80° C., 2 hours at 110° C., then further treated at 110° C./12 mm.Hg.; resulted in 863 parts of modi-40 fied aminoester: Viscosity 2000 cP/25° C., 12.9% OH, acid number 0.6, 3.34% N.

#### A 23

800 parts of aminoester according to A 1; 88 parts of ethylene oxide introduced at 80° 45 C., 2 hours at 110° C., then 1 hour at 110° C./12 mm.Hg.; resulted in 852 parts of modified aminoester: 13.1% OH, acid number 1.8, 3.37% N. Viscosity 1980 cP/25° C.

#### A 24

800 parts of aminoester according to A 1, 50 112 parts of acrylonitrile added dropwise at 80° C., 4 hours at 80° C.; 4 hours at 120° C., 4 hours at 120° C./12 mm.Hg.; resulted in 841 parts of modified aminoester: Vis-55 cosity 1870 cP/25° C., 11.1% OH, acid number 8.7, 4.92% N.

#### A 25

1160 parts of aminoester according to A 2, 112 parts of 1:2 propylene oxide added dropwise at 75° C., 2 hours at 75° C., 2 hours at 75° C./12 mm.Hg.; resulted in 1230 parts of a modified aminoester: 7.9% OH, acid number 1.0, 2.19% N. Viscosity 1175 cP/25° C.

#### A 26

1500 parts of aminoester according to A 15, 130 parts of acrylonitrile added at 70° C., 2 hours 70° C., 2 hours at 70° C./12 mm.Hg.; resulted in 1513 parts of modified aminoester: OH-number 256, acid number 15.6, 4.55% N.

#### A 27

1558 parts of aminoester according to A 2 were mixed at 75° C with 138 parts of acrylonitrile, left for 2 hours at 80° C., and 2 hours at 80° C./12 mm.Hg.; resulted in 1611 parts of modified aminoester: Viscosity 1213 cP/25° C., 7.9% OH, acid number 3.3, 3.2% N.

#### A 28

560 parts of distilled train fatty acid (molecular weight 280; acid number 200), 424 parts of diethylene glycol, 294 parts of maleic acid anhydride, 170° C./30 mm.Hg.; 168 parts of propylamine were added dropwise at 40° C, 2 hours at 40° C; resulted in 1341 parts of aminoester: Viscosity 2240 cP/25° C.

#### A 29

1060 parts of diethylene glycol, 490 parts of maleic acid anhydride, 200° C./200 mm.Hg.; 365 parts of *n*-butylamine at 50° C., 4 hours at 50° C. 42 parts of hexamethylene diisocyanate were introduced dropwise at 60° C. into 365 parts of the aminoester; resulted in modified aminoester: Viscosity 5800 cP/25° C., 11.7% OH, acid number 2.8, 5.4% N.

#### A 30

500 parts of the product A 6 were reacted at 70° C. with 60 parts of benzyl chloride. The mixture was stirred for 8 hours at 100° C. and then evacuated for 15 minutes to 12 mm.Hg. at 120° C. A quaternised aminoester 100 was obtained in an amount of 559 parts. Viscosity 1845 cP/25° C.; OH number 143; acid number 10.

The following Examples illustrate the invention.

#### EXAMPLE 1.

124 parts of aminoester A 4 were dissolved in 124 parts of ethylacetate. 19.6 parts of a 45% ethyl acetate solution of an adduct of toluylene diisocyanate (2,4- and 2,6-isomers 110 in the ratio of 65:35) and trimethylol propane (NCO-content 17.6%) were then added and the mixture was immediately brushed on a

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95

support. The combination hardened within 30 minutes at room temperature into an elastic coating which was resistant to solvents.

Example 2.

30.3 parts of aminoester A 4 were mixed with 8.7 parts of toluylene diisocyanate according to Example 1 and immediately poured into moulds. After further heating for half an hour at 80° C., an elastic moulded element was

obtained which was resistant to solvents. Examples 3 to 15.

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The components indicated in Table 1) (the numbers being parts by weight) were mixed mechanically and the foamable mixture was placed in moulds, in which a hard foam 15 material formed with the physical properties indicated in Table 2).

TABLE 1

	A		В	С	D	E	F	G	H	I	K	L
3	50	A 1	50		145	_	1	6	0.3	_		
4	50	A 2		50	127		_	6	0.3			
5	70	A 5		30	177		_	6	0.3		3	_
6	70	A 11	30		109		0.5	6	0.3		_	
7	70	A 12		30	129	_	_	6	0.3	_		1.5
8	70	A 13	30		138	_	0.5	6	0.3	_	_	_
9	70	A 17	30		148			6	0.3	_	3	
10	70	A 18	30		140		_	6	0.3	2		<del></del>
11	100	A 22			148	_	_	6	0.3			<del></del>
12	100	A 23		-	149	_	<b></b>	6	0.3			
13	70	A 24	30		136	2		6	0.3		_	-
14	70	A 25		30	118			6	0.3	_	-	. –
15	70	A 27	30		118			6	0.3		1.5	_

## Re: Table 1

- A Aminoester as starting material
- B Propoxylated trimethylol propane (OH-number 380)
- C Polyester of adipic acid, phthalic acid anhydride, oleic acid and trimethylol propane (OH-number 380)
- D Diphenylmethane-4,41-diisocyanate
- E Methylmorpholine
- F Permethylated aminoethyl piperazine
- G Sodium-castor oil sulphate (50% water)
- H Polysiloxane-polyalkylene glycol ester
- I Ethyl morpholine
- K Dimethylbenzylamine
- L Permethylated diethylene triamine

TABLE 2

	A	В	С	D	Е
3	43	2.8	1.0	110	4.5
4	50	3.5	0.8	125	3.4
5	43	2.3	0.3	129	4.5
6	41	2.1	1.2	94	4.3
7	38	3.1	0.8	113	3.6
8	53	3.2	0.6	123	1.9
9	40	2.4	0.5	124	3.2
10	40	2.2	0.4	118	2.7
11	49	2.5	0.9	145	4
12	49	2.3	0.8	136	3.6
13	41	2.9	0.8	134	2
14	43	2.5	0.8	106	4.9
15	41	2.2	1.2	112	4.6

A	Weight per unit volume	$kg/m^3$
В	Compressive strength	kg/cm
С	Impact toughness	kg/cm
D	Hot bending strength	° C.
E	Water absorption	%

#### Example 16.

100 parts by weight of aminoester A 4 were intimately mixed with 0.2 part by weight of stannous octoate, 0.4 part by weight of methyl polysiloxane, 1.0 part by weight of paraffin oil and 2.6 parts by weight of water. After the subsequent addition, carried out while stirring, of 38 parts by weight of toluylene diisocyanate (65% of 2,4-isomer and 35% of 2,6-isomer), the clouding mixture was poured into moulds. A fine-pored elastic soft foam material was formed which has good tensile strength and breaking elongation and 15 a low residual pressure-deformation.

#### Example 17.

100 parts by weight of aminoester A 8 were intimately mixed with 0.2 part by weight of stannous octoate, 1.2 part by weight of a polysiloxane polyalkylene glycol ester and 2.6

parts by weight of water and then 40 parts by weight of toluylene diisocyanate (80% of 2,4-isomer and 20% of 2,6-isomer) were added while stirring. The mixture became cloudy after a short time and a soft fine-pored foam material was formed which had a good tensile strength and breaking elongation and a low residual deformation.

#### EXAMPLE 18.

100 parts of modified aminoester A 30 30 were mixed with 0.25 parts of stannous octoate, 1 part of paraffin oil and 2.6 parts of water. 37 parts of the toluylene diisocynates of Example 1 were added. The reaction mixture expanded and solidified in a mould to give a semi-elastic foam with fine pores which was distinguished by increased water absorption.

#### WHAT WE CLAIM IS:-

A process for the production of synthetic plastics, which comprises reacting at least one polyester containing active hydrogen atoms (as determined by the Zerewittenof method) with one or more organic polyisocyanates, wherein the polyester is the addition product of a primary or secondary amine to a double bond which is in the α;β-position to an ester group of an α,β-unsaturated polyester.

2. A process as claimed in claim 1, wherein a secondary amine is used which is the reaction product of a primary amine and an alkylene oxide or  $\alpha,\beta$ -unsaturated ester or a nitrile.

3. A process as claimed in claim 1, wherein the adduct of the amine with the ester is in the form of an alkylation product.

4. A process as claimed in any of claims 1 to 3, wherein a chain extender is also present in the reaction mixture.

5. A process as claimed in any of claims 1 to 3, wherein a cross-linking agent is present in the reaction mixture.

6. A process as claimed in any of claims 1 to 4, wherein the reaction mixture is foamed. 25

7. A process as claimed in claim 1, substantially as described with reference to any of Examples 1 to 17.

8. A process as claimed in claim 1, substantially as described with reference to Example 18.

9. Synthetic plastics, particularly foamed polyurethanes when produced by the process claimed in any of the preceding claims.

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